# Materials for Devices: Problem Set 3

9. From Fick's first law, we have that under an applied voltage $V$, the current density obeys:

$$j_x = -qD\frac{\partial n}{\partial x} - \sigma\frac{\partial V}{\partial x},$$

where $n$ is the concentration of diffusing ions, $q$ their charge, $D$ is the diffusion coefficient, and $\sigma$ is the conductivity.

(i) Sketch a one-dimensional energy landscape for ionic diffusion, labelling the energy barrier $E_\mathrm{B}$.

(ii) Sketch the same one-dimensional energy landscape, but now in the presence of an external constant electric field such that there is a voltage difference $\Delta V$ between ionic sites.

(iii) Show that, in the presence of an external constant electric field, the net probability $p$ of a jump from one site to the other is proportional to:

$$p \propto e^{-\frac{E_\mathrm{B}}{k_\mathrm{B}T}}\left(1 - e^{-\frac{q\Delta V}{k_\mathrm{B}T}}\right)$$

(iv) Consider the limit of a small applied electric field, such that $q\Delta V \ll k_\mathrm{B}T$. Show that, in this limit, the net probability $p$ of a jump from one site to the other can be approximated as:

$$p \propto e^{-\frac{E_\mathrm{B}}{k_\mathrm{B}T}}\left(\frac{q\Delta V}{k_\mathrm{B}T}\right).$$

(v) Therefore, show that:

$$\frac{\partial n}{\partial x} = -\frac{nq}{k_\mathrm{B}T}\frac{\partial V}{\partial x}.$$

(vi) Hence, prove the validity of the Nernst-Einstein equation:

$$\frac{\sigma}{D} = \frac{nq^2}{k_\mathrm{B}T}.$$

10. (i) Sketch a unit cell of $CaF_2$ and describe the coordination of calcium by fluorine and of fluorine by calcium.

(ii) In $\delta$-$Bi_2O_3$, the bismuth sublattice is the same as that of calcium in $CaF_2$, but the stoichiometry means that there are vacant anion sites, randomly distributed. Sketch a possible unit cell of $\delta$-$Bi_2O_3$.

(iii) Explain why $\delta$-$Bi_2O_3$ is a fast ionic conductor whilst stoichiometric $CaF_2$ is not. How many oxygen vacancies are there, on average, per unit cell?

(iv) Consider yttria-stabilised zirconia, $Y_2O_3$ doped with $ZrO_2$, $Zr_{1-x}Y_xO_{[2-(x/2)]}$. Calculate the composition of yttria-stabilised zirconia which would give one quarter of the average oxygen vacancy content of $\delta$-$Bi_2O_3$.

11. Yttria stablilised zirconia with a cation ratio of 8:92 (Y:Zr) is produced by mixing appropriate quantities of yttria ($Y_2O_3$) with zirconia ($ZrO_2$). What is the molar oxygen composition, $x$, in the resulting material, $Y_{0.08}Zr_{0.92}O_x$?

12. The diffusivity of an ionic conductor is given by the Arrhenius equation $D = D_0 e^{-E_B/k_B T}$, where $E_B$ is the energy barrier, $D_0$ is the pre-exponential factor, and $T$ is the temperature.

    (i) In the limit of a good ionic conductor, the concentration of diffusing ions $n$ can be approximated as the total equilibrium concentration of ions $n \approx n_0$. Using this approximation in the Nernst-Einstein equation, show that:

    $$\ln \sigma \simeq \ln\left(\frac{\sigma_0}{T}\right) - \frac{E_B}{k_B T}, \tag{1}$$

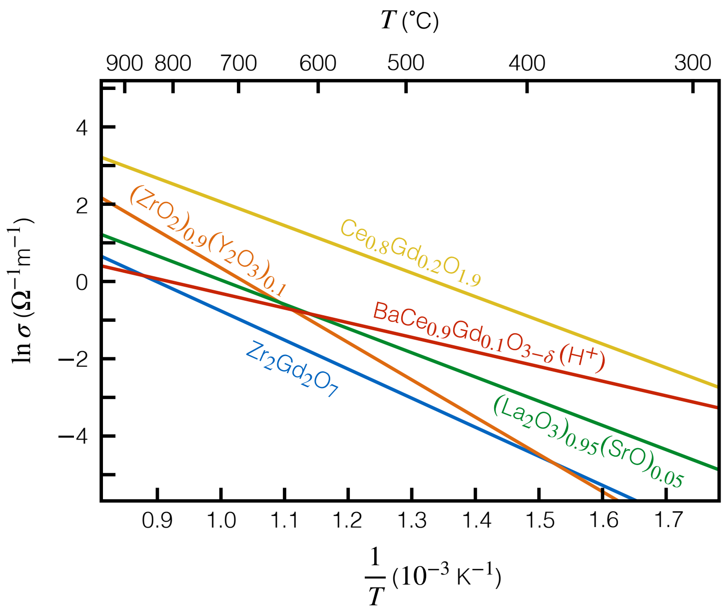
    where $\sigma_0 = \frac{D_0 n_0 q^2}{k_B}$.

    (ii) Consider the two terms on the right hand side of Eq. (1). By comparing their change between two characteristic temperatures for ionic conductor operation, for example between 700 K and 1000 K, argue that $\ln\left(\frac{\sigma_0}{T}\right)$ varies more slowly than $-\frac{E_B}{k_B T}$. Therefore, explain how a plot of $\ln \sigma$ against $\frac{1}{T}$, called an Arrhenius plot, can be used to understand the behaviour of ionic conductors.

    (iii) Consider the Arrhenius plot shown in the Figure below. Estimate the activation energy for ion transport in yttria-stabilised zirconia.

    (iv) In $Zr_{0.8}Y_{0.2}O_{1.9}$, how many oxygen vacancies are there per unit cell? If the lattice parameter of cubic yttria-stabilised zirconia is 0.54 nm, calculate the number of vacancies per unit volume.

    (v) The Nernst-Einstein equation indicates that the ratio $\frac{\sigma}{D}$ for a given material varies only with temperature. Calculate $\frac{\sigma}{D}$ for $Zr_{0.8}Y_{0.2}O_{1.9}$ at 800 °C.




13. The $\alpha$ phase of silver iodide (AgI) has a iodine atoms arranged in a body centred cubic lattice with $a = 5.0855$ Å for the conventional cubic cell. It is an ionic conductor with $Ag^+$ cations being the mobile species, and the diffusivity at 150 °C is $4.5 \times 10^{-11}$ m$^2$s$^{-1}$. A potential difference is applied across a sample of AgI, using Ag for both electrodes, and

current is allowed to flow. The half cell reactions are:

$$\begin{aligned} \text{cathode (reduction):} \quad & Ag^{+} + e^{-} \longrightarrow Ag \\ \text{anode (oxidation):} \quad & Ag \longrightarrow Ag^{+} + e^{-} \end{aligned}$$

Consider:

(i) What is the number of charge carriers per unit volume in AgI?

(ii) What is the conductivity of AgI at 150 °C?

(iii) What is the mass of silver deposited at the cathode if a current of 5 mA flows through the circuit for 5 minutes?